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Order-disorder transitions in polymer-surfactant systems

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We report on time resolved combined differential scanning calorimetry, small-angle and wide-angle x-ray scattering of hydrogen bonded flexible polymer-surfactant systems. The results show the presence of an order-disorder transition from a homogeneous to a lamellar structure due to dynamic coupling between surfactant and polymer. The homogeneous state exhibits a distinct small-angle x-ray scattering peak due to characteristic comb copolymerlike fluctuations. The peak position is strongly dependent on temperature and on the amount of surfactant material. [S1063-651X(96)11712-8]

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INTRODUCTION

Polyelectrolyte-surfactant systems [1–3], including gels, [4] have been studied extensively in recent years and it is now well established that these systems can give rise to extremely well ordered mesoscopic structures. In all cases investigated so far, the structures turn out to be stable in the temperature range studied and order-disorder transitions (ODT) are not observed nor is the possibility discussed. Polyelectrolyte-surfactant systems are characterized by a strong association between the head group of the surfactant and the corresponding group of the polymer. Furthermore, large unfavorable polar-nonpolar interactions exist between the nonpolar tail of the surfactant molecules and the rest of the system. These highly unfavorable interactions promote mesomorphic structures but prevent an ODT from occurring under normal conditions. The presence of an ODT in associated polymer-surfactant systems requires a delicate balance between the association interaction and the polar-nonpolar repulsion. In the mesomorphic state, the association has to compensate for the unfavorable free energy (stretching and interface interactions) of the microphase separated state, otherwise the structure will simply dissociate and possibly macrophase-separate. Ionic interactions are strong enough, but the presence of the charges also renders a transition to a homogeneous state highly unlikely.

Mesomorphic structures due to hydrogen bonding in polymer-surfactant systems have been realised only very recently [5–7]. Here we will demonstrate that an order-disorder transition occurs in our model system of poly(4-vinyl pyridine) (P4VP) and pentadecylphenol (PDP), and argue that it should be rather common in these types of polymer-surfactant systems involving hydrogen bonding. Above the ODT the homogeneous state still exhibits a characteristic small-angle x-ray scattering (SAXS) peak in analogy with conventional comb copolymers [8–10].

Of all systems exhibiting self-assembly, polymer-surfactant systems consisting of flexible polymers together with long tail surfactants offer unique opportunities to study systematically the influence of the composition of these comblike structures (i.e., the number of surfactant molecules per polymer repeat unit) on the order-disorder transition temperature as well as on the morphology and the transition between different morphologies. But perhaps more importantly, their behavior involves elements related to the dynamic surfactant-polymer equilibrium that are not present in ordinary comb copolymers. Depending on the two most important interactions in the problem, (i) the strength of the surfactant head–polymer interaction and (ii) the repulsion between the nonpolar alkyl tail and the polar polymer structure, we can in principle distinguish four different regimes. If the association interaction is strong enough, microphase separation occurs, provided the repulsion is also strong enough. As mentioned above, this is typically the case for the polyelectrolyte-surfactant systems studied so far, and will be called regime I. If the repulsive interaction is somewhat weaker but the association is still strong enough, microphase separation from a homogeneous to a microphase-ordered state may occur at a certain temperature, i.e., the order-disorder transition temperature. Above this temperature, the system is homogeneous showing a distinct SAXS peak due to the characteristic block copolymerlike fluctuations. This last case corresponds to regime II. In this paper we will present results on a particular polymer-surfactant system consisting of P4VP and PDP involving hydrogen bonds and show that there both regimes I and II are present. If the association becomes weaker, a SAXS peak will no longer be present, however, the system may still be homogeneous. This situation resembles ordinary mixtures. We call this regime III and list some explicit examples. Finally, if the association interaction becomes too weak to compensate, together with the entropy of mixing involved, for the polar-nonpolar repulsion, macrophase separation will occur in regime IV. This regime occurs usually for surfactants from regime III by increasing the alkyl length of the surfactant.

The presence of a SAXS peak in the otherwise homogeneous state, denoted as regime II, requires the characteristic lifetime of the hydrogen bonds to be at least of the same

order as the relaxation time of the concentration fluctuations giving rise to the peak. The correlations that give rise to the peak are due to the dynamic comblike structures, which therefore have to be permanent on the relevant time scale. From random phase approximation (RPA) calculations on model comb polymers, i.e., polymers comprising permanent side chains, we know that the characteristic wave vector q^* satisfies [11]

$$q^*\langle r^2\rangle^{1/2}\cong 2, \tag{1}$$

where

$$\langle r^2\rangle=(n_a+n_b)l^2, \tag{2}$$

Here, n_a and n_b are the number of segments per comb and per section of polymer chain between two successive combs located evenly along the chain. In these model calculations all segments have equal size l and random walk statistics is applied to both sections. Under these conditions, the wavelength of the dominant fluctuation is the sum of two contributions corresponding to the random walk size of the comb and the random walk size of the main chain section in between the combs. Increasing the number of combs obviously reduces this latter contribution, i.e., lateral fluctuations of the main chain become smaller in size, leaving the comb contribution intact. This ideal situation is not directly applicable to our model system P4VP-PDP, however, the physics underpinning these observations also holds in our case.

RESULTS AND DISCUSSION

The P4VP-PDP system has been investigated by combined time resolved SAXS, wide angle x-ray scattering (WAXS), and differential scanning calorimetry (DSC) at beamline 8.2 of the of the Synchrotron Radiation Source in Daresbury, England, using a beam of $\lambda=0.152$ nm x-rays measuring 3×0.3 mm^2 at the sample position [12]. The SAXS data were collected with a Daresbury quadrant detector. The WAXS data were acquired with a curved INEL detector and the DSC unit is a modified Linkham THM microscope hot stage. P4VP(PDP)$_x$ samples used, where x is the number of phenol groups per pyridine ring, had x values satisfying $0.15\leqslant x\leqslant 2.0$. The P4VP polymer used was acquired from Polyscience Europe GmbH and has a viscosity averaged molecular weight of $M_v=49\,000$ g/mol.

Figures 1 and 2 show the SAXS results as a function of temperature during slow cooling (5 °C min^{-1}) from the melt at 100 °C to 0 °C for $x=0.85$ and 1.5, respectively. The most striking feature in Fig. 1 is the very strong increase in scattering around 60 °C. This process is accompanied by an exothermic DSC peak and, in separate optical microscopy measurements, by the appearance of optical birefringence. So, we are actually observing an order-disorder transition. Upon further cooling, a second transition occurs around 20 °C due to crystallization of the side chains (pure PDP has an equilibrium melting point of 45 °C, but crystallizes around 25 °C during cooling at 5 °C min^{-1}). This conclusion follows straightforwardly from the WAXS and DSC data taken simultaneously. Although not clearly visible, a second order peak becomes present directly below the ODT. Its position at twice the original angle strongly suggests a lamellar structure.

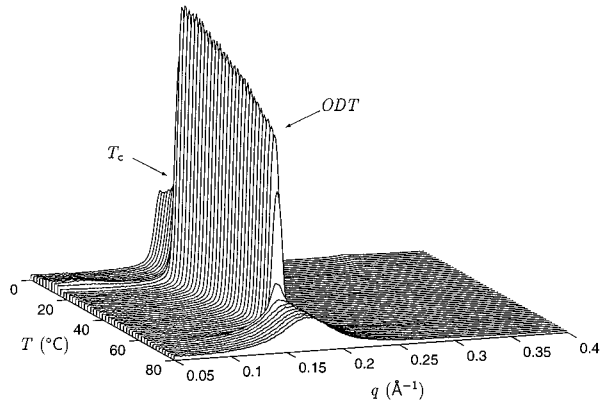

FIG. 1. SAXS patterns for P4VP(PDP)$_{0.85}$ during cooling with 5 °C min^{-1} from the melt at 100 °C.

The systems with a more than stoichiometric amount of surfactant molecules, i.e., $x\geqslant 1$, behave rather similarly. There are, however, important differences as well. In the case of $x=1.5$, the ODT occurs at a lower temperature around 25 °C and is followed immediately by crystallization of the side chains. The second order peak is now prominently present. For $x=2.0$, crystallization intervenes before the ODT is reached.

Figure 3 presents $2\pi/q^*$, where q^* is the wave vector at the peak position, as a function of x for a fixed temperature $T=80$ °C and at the actual order-disorder transition temperature, T_{ODT}, which itself depends on x as well. At 80 °C, $2\pi/q^*$ decreases monotonously as a function of x, a decrease that can be described quite well as a $1/x$ dependence. For x not too large this is well explained by the comb copolymer theory. In terms of the ideal model system, x corresponds to $1/n_b$ and then Eqs. (1) and (2) predict (for fixed n_a) an $1/x$ dependence for $n_a/n_b<1$. Of course, random walk statistics cannot be applied to the rather small sections of the main chain in between two successive hydrogen bound surfactants, and only as a very crude approximation to the alkyl tails consisting of 14 CH_2+1 CH_3 groups, but the basic physics remains valid even for this case. More difficult to explain is the continuing decrease of $2\pi/q^*$ for values of x

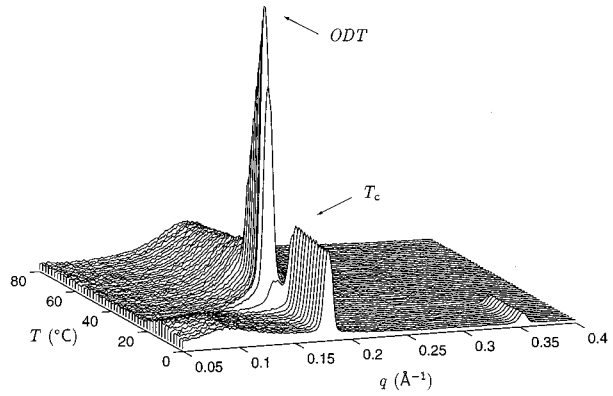

FIG. 2. SAXS patterns for P4VP(PDP)$_{1.5}$ during cooling with 5 °C min^{-1} from the melt at 100 °C.

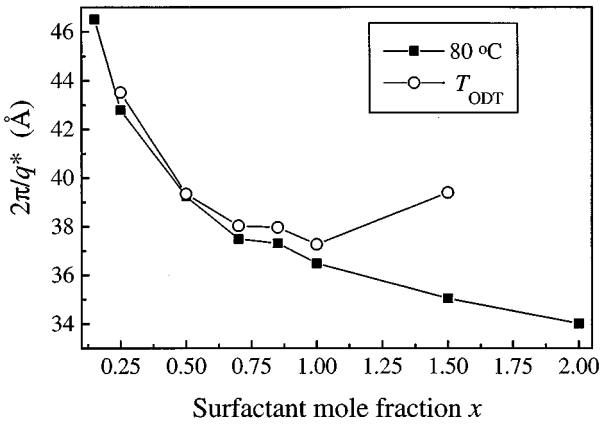

FIG. 3. $2\pi/q^*$ at 80 °C and at the order-disorder transition of P4VP(PDP)$_x$ as a function of x.

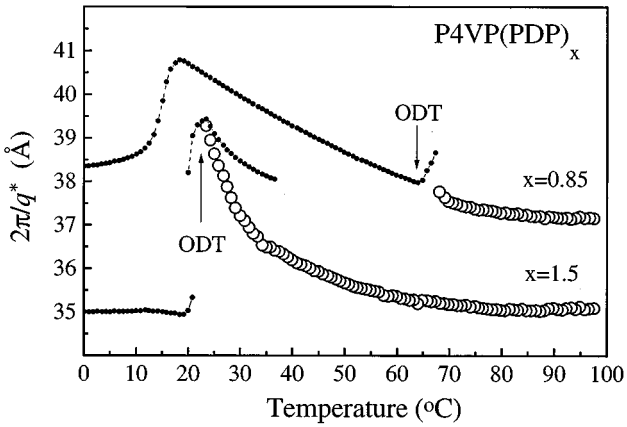

FIG. 4. $2\pi/q^*$ as a function of temperature for (a) $x=0.85$ and (b) $x=1.5$.

exceeding 1, unless we assume that the degree of association is smaller than 1 for $x=1.0$, as is to be expected, and that the degree of association continues to increase even up to $x=2.0$. At any rate, the results show that the characteristic fluctuations occur at a smaller length scale, most likely due to suppressed lateral fluctuations of the polymer backbone.

At the ODT, $2\pi/q^*$ decreases similarly for $0.15 \leqslant x \leqslant 1.0$. However, for $x=1.5$ it increases again, whereas for $x=2.0$, the ODT cannot be determined due to intervening alkyl crystallization. This change in behavior can be explained in the following way. Whereas for $T=80$ °C, only the polymer backbone together with the hydrogen bound surfactant molecules determine the size of the fluctuations, at the ODT the wavelength of the critical fluctuations represents the periodicity of the microphase separated structures that are being formed. The latter consist of almost fully complexed polymer molecules forming alternating layers of polar material and nonpolar alkyl material. The structure resembles lamellar microemulsions consisting of water, oil, and surfactant layers, where the role of water is taken by the P4VP polymers. The free uncomplexed surfactant molecules are apparently situated in between the brushlike structures much like the free homopolymer in the case of diblock copolymer systems. For $0.15 \leqslant x \leqslant 1.0$, the $1/x$ dependence of $2\pi/q^*$ at 80 °C and of the long period at 25 °C (before crystallization) had been observed before using conventional SAXS [7,13]. However, at that time we were not aware of the possibility of an order-disorder transition in these type of systems.

Figure 4 shows $2\pi/q^*$ as a function of temperature for $x=0.85$ and 1.5. Approaching the ODT from above, the microphase separated and the homogeneous structure are both present. Around 25 °C the alkyl layer crystallizes accompanied by a sudden decrease of $2\pi/q^*$. For $x=0.85$ the decrease is approximately 0.2 nm from 4.08 to 3.87 nm. Since the difference in density between the amorphous and crystalline phase of alkyl-like material is around 10%, and the alkyl layer represents approximately 50% by volume of the system, this reduction is very reasonable. For the $x=1.5$ case the reduction is considerably larger, around 0.45 nm. Apparently, during crystallization the free surfactant molecules are expelled from the crystalline alkyl layer formed by the hydrogen bound surfactant molecules. We did not observe any other sign of macrophase separation in P4VP(PDP)$_x$ for $x=1.5$ as well as for $x=2.0$ during the time resolved SAXS and WAXS measurements. Crystallization of pure PDP would be visible in the WAXS spectra, since pure PDP has a WAXS pattern (two characteristic 110 and 200 reflections) that is distinctively different from the crystalline alkyl layer in P4VP-PDP (only 1 peak at the 110 position) [7]. However, signs of macrophase separation are present after prolonged annealing at room temperature supporting the assertion that during the crystallization process, the free surfactant molecules are expelled from the crystalline structures.

Figure 5 presents the order-disorder transition temperature as a function of x. The data indicate that a maximum occurs around $x=0.85$ at approximately 63 °C. For more than stoichiometric amounts of surfactant, the transition temperature seems to drop fast based on the $x=1.5$ result. As indicated before, the $x>1.0$ case resembles block copolymer–homopolymer blends, where homopolymer chemically identical to one of the blocks is added to a block copolymer system. For diblock copolymers, this situation has recently be discussed in great detail by Matsen [14]. High molecular weight homopolymers tend to order the system, whereas low molecular weight homopolymers tend to disorder microstructures. For comb copolymers a similar analysis has not

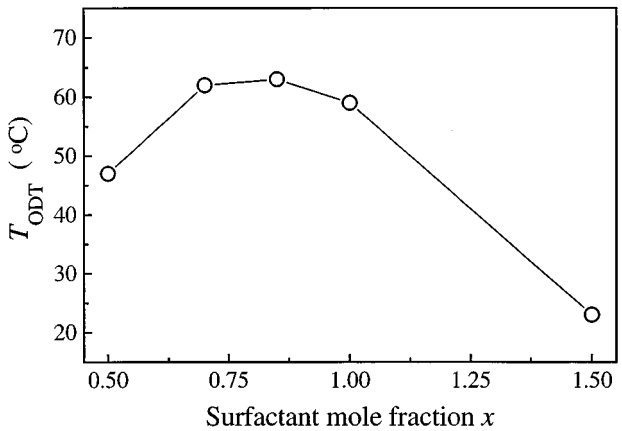

FIG. 5. Order-disorder transition temperature of P4VP(PDP)$_x$ as a function of x, as observed during cooling with 5 °C min^{-1} from the melt at 100 °C.

yet been presented and even if it were available, our systems still differ considerably due to the presence of highly polar head groups. Theoretically, the order-disorder transition temperature of pure comb copolymers is a strong function of the volume fraction of combs ν in the system, reaching a maximum at $\nu \cong 0.6$ [11]. In our case, values of $x \leqslant 1.0$ correspond to volume fractions of alkyl chains approximately equal to (using the same notation) $\nu \leqslant 0.58$ [7]. Hence, the decrease in transition temperature for decreasing values of x should come as no surprise.

CONCLUDING REMARKS

We introduced four different regimes in the beginning of this paper. As indicated, ionic surfactants lead almost invariably to regime I (i.e., microphase separated structures) due to the strong repulsion involved. A specific alkyl phenol surfactant PDP combined with P4VP is demonstrated here to be in regime I or II depending on the temperature. It is not unreasonable to expect that this will remain true for various other alkyl phenol surfactants in combination with P4VP. Since, in spite of its dynamic nature, the hydrogen bonding is apparently strong enough, whether or not an order-disorder transition will occur depends largely on the repulsive interaction between the alkyl tail and the rest of the system. This in turn is related to the polarity of the polymer-surfactant head structure, which will be similar for phenol type surfactants. Meanwhile we have investigated a series of surfactants with different (weaker) hydrogen bonding strength together with our model polymer P4VP and found that alkyl carboxylic acid surfactants with alkyl tails from 11 to 18 carbon atoms are in regime II, and alkyl aliphatic alcohols are in regime III up to dodecanol and in regime IV for hexadecanol and higher [15]. In particular the observation that P4VP-dodecanol forms a homogeneous mixture characterized by a conventional SAXS spectrum, i.e., a monotonously decreasing scattering as a function of the scattering angle, demonstrates the important role of the average lifetime of a hydrogen bond for the occurrence of a comb copolymerlike scattering peak at finite nonzero scattering angle. This lifetime has to be long enough to induce concentration fluctuations largely determined by the polymer-surfactant conformations. This range of behavior as a function of the association strength opens the way for new theoretical developments taking the dynamic nature of the association, and hence the different time scales involved, explicitly into account. Preliminary computer simulations indicate that, as a function of the surfactant head–polymer interaction, a sudden transition to a comb copolymerlike scattering occurs [16].

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